EPR study of fine and hyperfine interactions of Gd^{3+} in $Bi_{2(1-x)}Gd_{2x}Se_3$ and $Pb_{1-x}Gd_xSe$

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Electron paramagnetic resonance experiments were performed on $Bi_{2(1-x)}Gd_{2x}Se_3$ and $Pb_{1-x}Gd_xSe$ samples at room and liquid-helium temperatures. The Gd^{3+} sites are characterized by hexagonal and octahedral symmetries in $Bi_{2(1-x)}Gd_{2x}Se_3$ and $Pb_{1-x}Gd_xSe$ samples, respectively. The absolute signs of the spin-Hamiltonian parameters in $Bi_{2(1-x)}Gd_{2x}Se_3$ were determined by comparing the intensities of the lines at room and liquid-helium temperatures: $b_2^0<0$, $b_4^0>0$, and $b_6^0<0$. The $|b_2^0|$ value in $Bi_{2(1-x)}Gd_{2x}Se_3$ increased nonlinearly with decreasing temperature, becoming constant below 40 K. At the low temperature of 2.2 K, four hyperfine transitions due to the ^{155}Gd isotope ($I=3/2$) were observed in $Pb_{1-x}Gd_xSe$, leading to the average value of the hyperfine-coupling constant of 2.55 ± 0.10 mT for the two ^{155}Gd and ^{157}Gd processing nonzero nuclear magnetic moments. [S0163-1829(97)08109-5]

I. INTRODUCTION

Many researches involving electron paramagnetic resonance (EPR) and magnetic properties on diluted magnetic semiconductors have been reported in the literature.[1–5] Recently, some of us published studies on magnetic properties of $Bi_{2(1-x)}Ge_{2x}Te_3$ ($x=0.01$).[6,7] It was found that the magnetizations at 4.2 and 1.8 K fit very well with contributions both from isolated Gd^{3+} ions and their pairs. The exchange interaction between the Gd^{3+} ions was determined to be antiferromagnetic, with the value $J_P/k_B=-0.5$ K.

Bi_2Te_3 and Bi_2Se_3 single crystals are semiconductors, characterized by small indirect gaps $E_g=150$ and 160 meV for Bi_2Te_3 and Bi_2Se_3, respectively.[8] Both these materials possess rhombohedral structure ($R3m$).[7,8] The characteristic cleavage planes result due to the shorter interlayer bond lengths between the Se atoms. The layers alternate in the following sequence of planes perpendicular to a threefold axis: $Se^{(1)}$-Bi-$Se^{(2)}$-Bi-$Se^{(1)}$. As for PbSe, it is a IV-VI semiconductor, characterized by a small gap $E_g=300$ meV at room temperature.[9–11]

Recently, magnetization measurements on rare-earth-ion-doped PbSe (Eu^{2+},Gd^{3+}) samples were reported.[2,12,13] In this material, the first-nearest-neighbor exchange interaction is the dominant one. The exchange interactions among the rare-earth ions in IV-VI semiconductors are much smaller in comparison to those characterizing II-VI semiconductors. A recent low-temperature magnetization measurement on three samples of $Pb_{1-x}Eu_xSe$ ($x=1.3\%$, 3.0%, and 4.1%) revealed the existence of an antiferromagnetic exchange constant $J_1/k_B=-0.24\pm0.02$ K between the Eu^{2+} ions.[2] Magnetization steps due to single-ion anisotropy of the Eu^{2+} ion in PbSe confirmed the positive absolute sign of b_4^0. In addition, the value of b_4^0 so estimated was found to be in good agreement with that estimated by EPR.[1] The first EPR studies on $Pb_{1-x}Gd_xSe$ were performed by Bacskay *et al.*[14] at room temperature. In this paper, room- and liquid-helium-temperature EPR measurements on the Gd^{3+} ion incorporated in Bi_2Se_3 and PbSe samples are presented.

II. SAMPLE PREPARATION AND EXPERIMENTAL ARRANGEMENT

$Bi_{2(1-x)}Gd_{2x}Te_3$ and $Pb_{1-x}Gd_xSe$ samples were prepared by the well-known Bridgman technique. Mixtures of constituting elements, each of 99.999% purity, were used in a sealed evacuated quartz ampoule at a constant temperature of 850 °C for 72 h. The Bridgman apparatus was characterized by a temperature gradient of about 20 °C/cm. The unit-cell parameters were determined by x-ray diffraction for hexagonal Bi_2Se_3 to be $a=4.14$ Å and $c=28.7$ Å, and, for cubic PbSe, $a=6.12$ Å. The microprobe analysis revealed the concentration (x) of Gd^{3+} ions to be 0.12% and 1.04% in $Bi_{2(1-x)}Gd_{2x}Te_3$ and $Pb_{1-x}Gd_xSe$, respectively. A Bruker spectrometer (9.58 GHz) equipped with an Oxford helium-gas-flow cryostat to attain liquid-helium temperatures and a Varian spectrometer (9.14 GHz) equipped with a commercial (Andonian) helium-immersion cryostat, wherein the temperature 2.2 K was obtained by pumping on liquid helium were used for EPR measurements. The $Bi_{2(1-x)}Gd_{2x}Se_3$ sample, with approximate dimensions $0.5\times2\times4$ mm^3, was placed in an evacuated, sealed quartz tube.

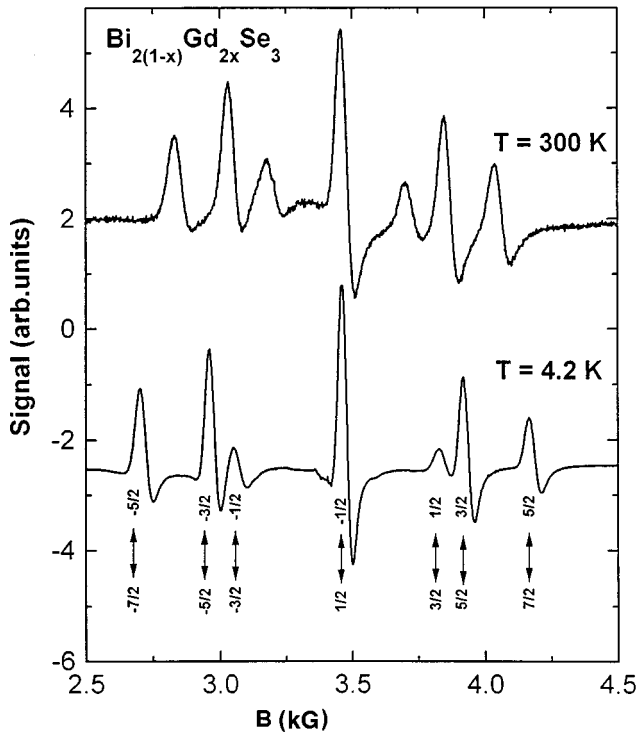

FIG. 1. X-band (9.57 GHz) EPR spectra of $Bi_{2(1-x)}Gd_{2x}Se_3$ at 300 and 4.2 K, the external magnetic field being parallel to the c axis. The difference in the overall splittings at the two temperatures can be clearly seen.

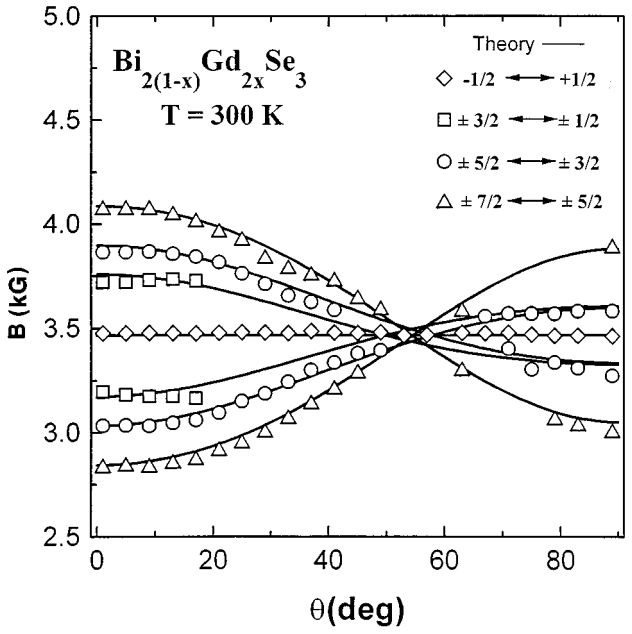

FIG. 2. Angular variation of the positions of the allowed Gd^{3+} fine-structure EPR lines ($\Delta M=\pm 1$) at 300 K in $Bi_{2(1-x)}Gd_{2x}Se$, the external magnetic-field orientation being parallel to the c axis ($\theta=0°$). Discrete symbols exhibit experimental data, while the solid lines represent calculated line positions.

III. EXPERIMENTAL RESULTS AND DISCUSSION

A. Gd^{3+} in Bi_2Se_3

1. Spin Hamiltonian and line positions

The Gd^{3+} spin Hamiltonian appropriate to the hexagonal site symmetry in Bi_2Se_3 and assuming an isotropic g matrix, since the departures from isotropic symmetry are small is given, in the usual notation by[15–18]

$$\mathcal{H}=g\mu_B\mathbf{B}\cdot\mathbf{S}+\tfrac{1}{3}b_2^0O_2^0+\tfrac{1}{60}(b_4^0O_4^0+b_4^3O_4^3)+\tfrac{1}{1260}(b_6^0O_6^0+b_6^3O_6^3+b_6^6O_6^6). \quad (1)$$

The positions of the lines to second order in perturbation for **B** parallel to the hexagonal axis are given in Refs. 15–17.

2. EPR spectra

The EPR spectrum of $Bi_{2(1-x)}Gd_{2x}Se_3$ was recorded at various temperatures for $\mathbf{B}\|c$ axis. Figure 1 shows the EPR spectra at 300 and 4.2 K, exhibiting seven allowed transitions corresponding to $\Delta M=\pm 1$. The peak-to-peak average width of the first-derivative line shape at room temperature was about 60 G, decreasing to 40 G at 4.2 K. The line shapes of the observed transitions were Dysonian due to the skin effect caused by the high conductivity of the material.[16,18] Electrical-transport measurements at room temperature revealed that the sample was a n-type superconductor with carrier concentration $n=2.1\times10^{19}$ and resistivity $\rho=4.8\times10^{-4}\ \Omega$ cm. The observed increase in the intensities of the lines at 4.2 K at low fields compared to those at high fields relative to the intensities at 300 K yielded the absolute signs $b_2^0<0$, $b_4^0>0$, and $b_6^0<0$.[15] As a result of the rather large linewidth (4 mT) which masked this variation, it was very difficult to estimate the values of the parameters b_6^3 and b_6^6, which are responsible for expected small variation of line position for $\mathbf{B}\perp c$ axis with good accuracy. The values of all parameters, except for b_6^3 and b_6^6, as estimated from line positions at 300 and 4.2 K are listed in Table I. In Fig. 2 are exhibited the EPR line positions in $Bi_{2(1-x)}Gd_{2x}Se_3$ at various orientations of **B**. Figure 3 shows a plot of the values of the spin-Hamiltonian parameters b_2^0, b_4^0, and b_6^0 as functions of temperature, similar to that observed in $KZnF_3$ and PbGdTe.[19,20] The temperature variations of b_m^0, $m=2,4,6$, were fitted theoretically to the following nonlinear expression in temperature:[21]

$$b_m^0(T)=b_m^0(0)[1-CT^n]. \quad (2)$$

TABLE I. Fine-structure spin-Hamiltonian parameters for Gd^{3+} in $Bi_{2(1-x)}Gd_{2x}Se_3$ single crystal at 300 and 4.2 K. Here Δ represents the overall splitting in zero magnetic field $\Delta=12b_2^0-2b_4^0+6b_6^0$.

T (K)	g	b_2^0 (GHz)	b_4^0 (GHz)	b_4^3 (GHz)	b_6^0 (GHz)	Δ (GHz)
300	2.001±0.005	−0.293±0.004	0.0052±0.0004	0.0033±0.0001	−0.0066±0.0004	−3.57±0.049
4.2	1.998 ± 0.005	−0.349 ± 0.01	0.011 ± 0.0002	0.0031 ± 0.0002	−0.015 ± 0.0002	−4.35 ± 0.12

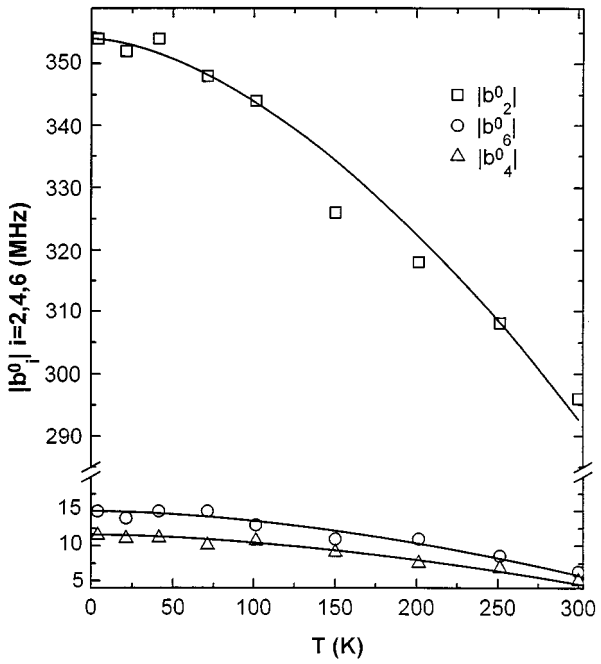

FIG. 3. The spin-Hamiltonian parameters b_2^0, b_4^0, and b_6^0 plotted as functions of temperature for Gd^{3+} in Bi_2Se_3. Discrete symbols exhibit data, while the solid lines are those calculated by use of Eq. (2).

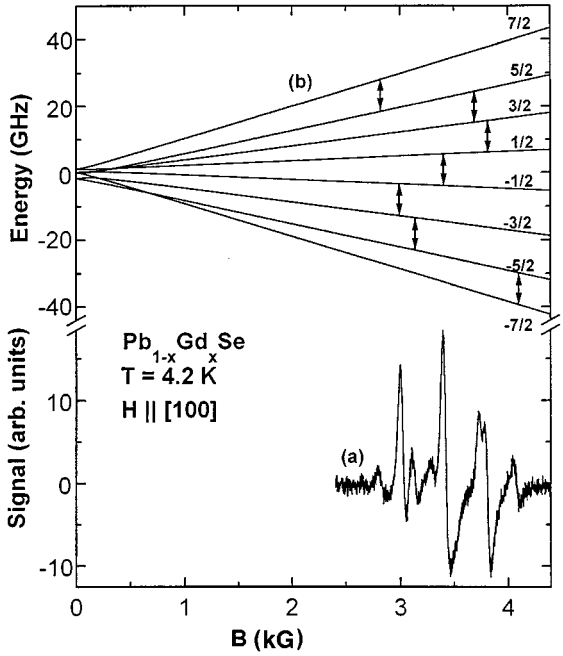

FIG. 4. (a) Plots of the Gd^{3+} EPR spectrum at 4.2 K in a single crystal of $Pb_{1-x}Gd_xSe$ ($x \sim 0.01$) and (b) the energy levels as calculated by a numerical diagonalization of the spin-Hamiltonian matrix as functions of the intensity of the external magnetic field, whose orientation is parallel to the [100] direction.

Here $b_m^0(0)$ and $b_m^0(T)$ are the values of the parameter b_m^0 at 0 K and T, respectively, with $b_m^0(0)$ assumed to have the same value as that at 4.2 K. The $[C,n]$ are [1.5,1.64], [5.0,1.65], and [4.6,1.69], respectively, for b_2^0, b_4^0, and b_6^0.

The coefficient α that represents the admixture between the $^8S_{7/2}$ and $^6P_{7/2}$ states has been estimated as 0.12 from the g value as follows:[15,20]

$$g=(1-g\alpha^2)g_S+\alpha^2 g_P, \tag{3}$$

with $g_S=2.0023$ and $g_P=1.716$ being the Landé factor for the $^8S_{7/2}$ and $^6P_{7/2}$ states, respectively, and $g=1.998$ as estimated presently at 4.2 K.

B. Gd^{3+} in PbSe

1. Spin Hamiltonian

The $^8S_{7/2}$ state of the gadolinium ion splits in the octahedral site symmetry of PbSe into two doublets Γ_6 and Γ_7 and one quadruplet Γ_8, which lies between the two doublets. The Γ_6 state belongs to the lowest energy leading to a positive sign of the spin-Hamiltonian parameter b_4^0.[1,15] The Gd^{3+} spin Hamiltonian in cubic site symmetry is, in the usual notation and including the hyperfine interaction[15–17]

$$\mathcal{H}=g\mu_B\mathbf{B}\cdot\mathbf{S}+\tfrac{1}{60}b_4(O_4^0+5O_4^4)+\tfrac{1}{1260}b_6(O_6^0-21O_6^4)+A\mathbf{I}\cdot\mathbf{S}. \tag{4}$$

2. EPR spectra

No EPR spectra could be observed at 300 K due to the skin effect, which eliminates the signal entirely. Figure 4(a) shows the EPR spectra of Gd^{3+} in $Pb_{1-x}Gd_xSe$ at 4.2 K, while Fig. 4(b) shows the transitions between the energy levels corresponding to the EPR lines in Fig. 4(a).

At low temperatures, the central transition splits into four hyperfine transitions corresponding to $(2I+1)$ components of the nuclear magnetic moment of the ^{155}Gd isotope. The gadolinium ion has two isotopes ^{155}Gd and ^{157}Gd, with nonzero nuclear magnetic moments 0.32 (abundance 14.8%) and 0.24 (abundance 15.6%), respectively, each characterized by

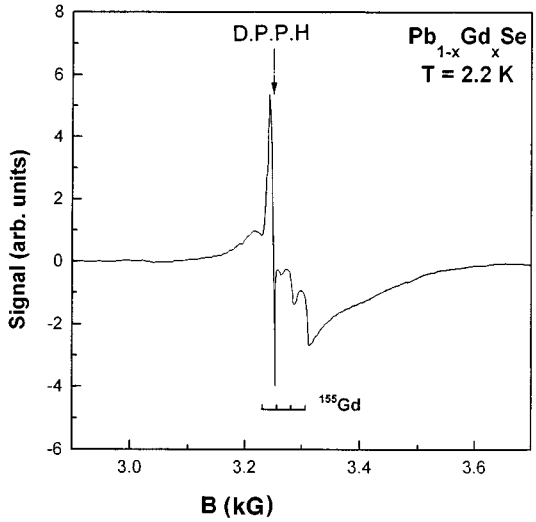

FIG. 5. Gd^{3+} EPR spectrum in $Pb_{1-x}Gd_xSe$ powder at 2.2 K. The central $+1/2 \leftrightarrow -1/2$ transition for the ^{155}Gd and ^{157}Gd isotopes (for each isotope $I=3/2$) splits clearly into four hyperfine transitions. However, the lines corresponding to the two isotopes cannot be distinguished from each other due to the rather large linewidths.

the nuclear spin $I=3/2$. The hyperfine (HF) interaction constant parameter A can be estimated from the HF splitting of the fine-structure central line $(M=+1/2\leftrightarrow-1/2)$: $(m=-3/2,\ -1/2,\ +1/2,\ +3/2$; m is the nuclear magnetic quantum number). From Fig. 5, displaying the X band (9.14 GHz) spectrum at 2.2 K, the hyperfine-coupling constant A was estimated to be 2.55 ± 0.1 mT, the average of the HF constants for the isotopes ^{155}Gd and ^{157}Gd, due to the nonresolution of the corresponding HF lines. The values of the fine-structure spin-Hamiltonian parameters as estimated from EPR line positions are $g=1.990\pm0.005$, $b_4=+92.0\pm2$ MHz, and $b_6=-1.0\pm2$ MHz at 4.2 K, the value of the admixture parameter α being 0.12 at 4.2 K as estimated by the use of Eq. (3).

IV. CONCLUDING REMARKS

From the present EPR measurements, it can be concluded that the Gd^{3+} ion substitutes at sites of hexagonal and octahedral symmetries in Bi_2Se_3 and PbSe, respectively. The spin-Hamiltonian parameters in Bi_2Se_3 were found to be temperature dependent; the $|b_2^0|$ value increased nonlinearly with decreasing temperature, attaining a constant value below 40 K. The EPR line shapes were Dysonian due to the high conductivity of the materials. The Gd^{3+} EPR spectrum, exhibiting hyperfine structures due to ^{155}Gd and ^{157}Gd isotopes, was observed in PbSe only at 2.2 K.

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